Electronic Supplementary Information for:

Tuning stoichiometry and supramolecular assembly in perfluorinated indazolato coinage metal complexes

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1. Experimental details

All reactions requiring inert atmosphere were carried out using Schlenk techniques or glovebox. The solvents were dried and distilled using the conventional methods, diethyl ether and tetrahydrofuran (Na/benzophenone), toluene (Na), dichloromethane, pentane and dimethoxyethane (CaH_2). The 3-pentafluoroethyl-4,5,6,7-tetrafluoro-1-H-indazole[1] and $[Cu(MeCN)_4][BF_4]$[2,3] were synthesized according to literature procedures. All other chemicals were used as purchased.

The NMR experiments were acquired at 298 K using a DPX300 Bruker and an AVANCE Bruker 400 MHz spectrometers. Elemental analysis and X-ray diffraction were carried out by the analytical service of our laboratory.

2. Synthesis of $\{[3\text{-}(C_2F_5)IndF_4]Ag\}_3$ [1]:

A suspension of Ag_2O (0.058 g, 0.25 mmol) and 3-pentafluoroethyl-4,5,6,7-tetrafluoro-1-H-indazole (0.152 g, 0.49 mmol) in dry toluene (10 ml) was heated to reflux for 4.5 h in a Schlenk flask covered with aluminum foil. The not yet cold solution was filtered through a bed of Celite to remove insoluble material. The filtrate was collected, and the solvent was removed under reduced pressure. The resulting solid was washed with pentane (2x5 ml) to yield $\{[3\text{-}(C_2F_5)IndF_4]Ag\}_3$ **[1]**·toluene as a white solid (0.200 g, 0.15 mmol, 90 % yield).

X-ray quality crystals were obtained by slow evaporation of an ether solution.

^{19}F-NMR (CD_2Cl_2, 282 MHz, 298 K) δ [ppm]: -84.7 (s, 3F, -C*F*$_3$), -112.2 (d, 2F, J_{FF} = 24.1 Hz, C*F*$_2$CF$_3$), -143.0 (m, 1F, F(4)), -157.1 (t, 1F, J_{FF} = 17.5 Hz, F(6)), -159.5 (m, 1F, F(7)), -162.8 (t, 1F, J_{FF} = 17.9 Hz, F(5)).

Anal. Calcd. for $\{[3\text{-}(C_2F_5)IndF_4]Ag\}_3$·toluene, $C_{34}H_8Ag_3F_{27}N_6$: C, 30.54; H, 0.60; N, 6.29. Found: C, 30.12, H, 0.83; N, 6.62.

3. Synthesis of [(toluene)(1)(toluene)]

[1]·toluene was dissolved in toluene. X-ray quality crystals of [(toluene)($\{[3\text{-}(C_2F_5)IndF_4]Ag\}_3$)(toluene)] were obtained by slow evaporation of the toluene solution in the Glove box.

4. Synthesis of $\{Cu_5[3\text{-}(C_2F_5)IndF_4]_6\}Et_3NH$ [2]

Et_3N (0.117 g, 1.15 mmol, 0.16 ml) was added to a suspension of $[Cu(MeCN)_4][BF_4]$ (0.2 g, 0.64 mmol) and 3-pentafluoroethyl-4,5,6,7-tetrafluoro-1-H-indazole (0.237 g, 0.77 mmol) in toluene (20 ml). The suspension turned yellow immediately. After stirring for 3 h at r.t., the

solvent was removed under vacuum. The resulting solid was then extracted with dry Et_2O (3x10 ml) and the extract filtered through a bed of Celite. After evaporation of the solvent, the solid was washed with dry pentane (2x5 ml) to yield $\{Cu_5[3\text{-}(C_2F_5)IndF_4]_6\}Et_3NH$ as an off-white solid (0.200 g, 0.09 mmol, 70% yield).

X-ray crystals were obtained by slow evaporation of an ether solution.

^{19}F-NMR (acetonitrile-d_3, 376 MHz, 298 K) δ [ppm]: -84.1 (s, 3F, CF_3), -108.1 (d, 2F, J_{FF} = 20.2 Hz, CF_2CF_3), -146.7 (s, 1F, F(4)), -159.5 (s, 1F, F(6)), -165.5 (t, 1F, J_{FF} = 17.0 Hz, F(7)), -169.7 (t, 1F, J_{FF} = 17.0 Hz, F(5)).

Anal. Calcd. for $C_{60}H_{16}Cu_5F_{54}N_{13}$: C, 31.85; H, 0.71; N 8.05. Found: C, 32.02; H, 0.71; N, 8.19.

5. Crystal data and structure refinement for 1 (Table S1)

Empirical formula	C_{27} Ag_3 F_{27} N_6, C_4 H_{10} O
Formula weight	1319.06
Temperature	180(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 12.6128(9) A alpha = 78.199(3) deg. b = 12.9362(5) A beta = 73.173(3) deg. c = 13.6226(7) A gamma = 63.132(4) deg.
Volume	1890.77(18) A^3
Z, Calculated density	2, 2.317 Mg/m^3
Absorption coefficient	1.712 mm^-1
F(000)	1260
Crystal size	0.2 x 0.12 x 0.03 mm
Theta range for data collection	3.38 to 26.37 deg.
Limiting indices	-15<=h<=15, -16<=k<=16, -17<=l<=17
Reflections collected / unique	31328 / 7710 [R(int) = 0.0432]
Completeness to theta = 26.37	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8779 and 0.6954
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7710 / 0 / 615
Goodness-of-fit on F^2	0.999
Final R indices [I>2sigma(I)]	R1 = 0.0310, wR2 = 0.0621
R indices (all data)	R1 = 0.0497, wR2 = 0.0687
Largest diff. peak and hole	0.803 and -0.500 e.A^-3

6. Crystal data and structure refinement for [(toluene)(1)(toluene)] (Table S2)

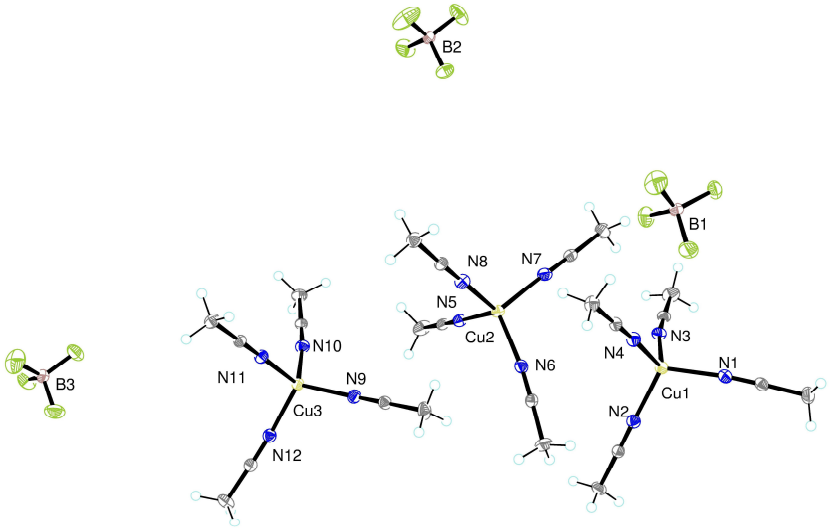
Empirical formula	C27 Ag3 F27 N6, 2(C7 H8)
Formula weight	1429.21
Temperature	180(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 12.5640(5) A alpha = 74.837(3) deg. b = 12.8440(4) A beta = 75.239(4) deg.

	c = 16.4240(7) A gamma = 60.808(4) deg.
Volume	2207.60(15) A^3
Z, Calculated density	2, 2.150 Mg/m^3
Absorption coefficient	1.474 mm^-1
F(000)	1376
Crystal size	0.15 x 0.12 x 0.1 mm
Theta range for data collection	3.36 to 26.37 deg.
Limiting indices	-15<=h<=15, -16<=k<=16, -20<=l<=20
Reflections collected / unique	26584 / 8997 [R(int) = 0.0549]
Completeness to theta = 26.37	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.987 and 0.895
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8997 / 6 / 696
Goodness-of-fit on F^2	1.096
Final R indices [I>2sigma(I)]	R1 = 0.0685, wR2 = 0.1474
R indices (all data)	R1 = 0.1017, wR2 = 0.1608
Largest diff. peak and hole	2.126 and -0.886 e.A^-3

7. Crystal data and structure refinement for 2 (Table S3)

Empirical formula	C_{54} Cu_5 F_{54} N_{12}, C_6 H_{16} N, C_4 H_{10} O
Formula weight	2336.68
Temperature	180(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P n a 21
Unit cell dimensions	a = 22.0065(12) A alpha = 90 deg.
	b = 13.1308(9) A beta = 90 deg.
	c = 27.0131(19) A gamma = 90 deg.
Volume	7805.8(9) A^3
Z, Calculated density	4, 1.988 Mg/m^3
Absorption coefficient	1.523 mm^-1
F(000)	4560
Crystal size	0.15 x 0.14 x 0.11 mm
Theta range for data collection	1.72 to 26.37 deg.
Limiting indices	-25<=h<=27, -16<=k<=16, -33<=l<=33
Reflections collected / unique	83406 / 15886 [R(int) = 0.0419]
Completeness to theta = 26.37	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.991 and 0.897
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	15886 / 30 / 1159
Goodness-of-fit on F^2	1.017
Final R indices [I>2sigma(I)]	R1 = 0.0479, wR2 = 0.1226
R indices (all data)	R1 = 0.0723, wR2 = 0.1390
Largest diff. peak and hole	1.198 and -0.667 e.A^-3

8.1. ORTEP view of $[Cu(CH_3CN)_4]BF_4$



8.2. Crystal data and structure refinement for $[Cu(CH_3CN)_4]BF_4$ (Table S4)

Empirical formula	$C_8 H_{12} Cu N_4, BF_4$
Formula weight	314.58
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P n a 21
Unit cell dimensions	a = 23.705(5) A alpha = 90 deg. b = 8.276(5) A beta = 90 deg. c = 20.188(5) A gamma = 90 deg.
Volume	3961(3) A^3
Z, Calculated density	12, 1.583 Mg/m^3
Absorption coefficient	1.688 mm^-1
F(000)	1896
Crystal size	0.2 x 0.15 x 0.08 mm
Theta range for data collection	1.99 to 36.37 deg.
Limiting indices	-37<=h<=39, -13<=k<=13, -32<=l<=25
Reflections collected / unique	95171 / 15924 [R(int) = 0.0213]
Completeness to theta = 25.00	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.985 and 0.876
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	15924 / 1 / 498
Goodness-of-fit on F^2	1.029
Final R indices [I>2sigma(I)]	R1 = 0.0238, wR2 = 0.0560
R indices (all data)	R1 = 0.0293, wR2 = 0.0575
Largest diff. peak and hole	0.472 and -0.306 e.A^-3

References:

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